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Synthesis, crystal structure and electrophysical properties of triple molybdates containing silver, gallium and divalent metals

A possibility of the triple molybdates formation with both NASICON-like and $NaMg_3In(MoO_4)_5$ structures in the Ag_2MoO_4–$AMoO_4$–$Ga_2(MoO_4)_3$ (A = Mn, Co, Zn, Ni) systems was studied by powder X-ray diffraction analysis. It was established that NASICON-like phases $Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3$ are not formed. The triple molybdates $AgA_3Ga(MoO_4)_5$ (A = Mn, Co, Zn) isostructural to triclinic $NaMg_3In(MoO_4)_5$ (sp. gr. $P\bar{1}$, Z = 2) were synthesized and characterized. The structure of the obtained compounds was refined for $AgZn_3Ga(MoO_4)_5$ according to the powder data by the Rietveld method. The structure consists of MoO_4 tetrahedra, couples of edge-shared $M(1)O_6$ octahedra, and trimers of edge-shared $M(2)O_6$–, $M(3)_6$– and $M(4)O_6$ octahedra, which are linked by the common vertices to form a 3D framework. High-temperature conductivity measurements revealed that the conductivity of $AgMn_3Ga(MoO_4)_5$ at 500 °C reaches 10^{-2} S/cm, which is close to one of the known NASICON-type ionic conductors.

Keywords: triple molybdates; silver; gallium; solid-state synthesis; powder X-ray diffraction; Rietveld refinement; ionic conductivity.

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Introduction

A synthesis and studying of complex oxide compounds, the development of new materials with functionally significant properties based on those are among the main areas of the materials science. An important place in the study and obtaining of new phases with valuable physicochemical properties belongs to molybdates, in particular triple ones, which are among the fastest-growing groups of complex oxide compounds containing a tetrahedral anion and three different cations. One of the largest families of these compounds is molybdates containing 1-, 2- and 3-charged cations. In particular, silver-containing NASICON-like phases

$Ag_{1-x}A_{1-x}R_{1+x}(MoO_4)_3$ (A = Mg Co, R = Al; A = Mg, R = In) with different homogeneity range and triclinic $AgA_3R(MoO_4)_5$ (A = Mg, R = Cr, Fe, Ga; A = Mn, R = Al, Cr, Fe, Sc, In) having high ionic conductivity (10^{-3}–10^{-2} S/cm) are of interest. For a number of phases: $AgMg_3R(MoO_4)_5$ (R = Cr, Fe), $AgMn^{II}_3$ $(Mn^{III}_{0.26}Al_{0.74})(MoO_4)_5$, $Ag_{0.90}Al_{1.06}Co_{2.94}(MoO_4)_5$ and $AgFe^{II}_3Fe^{III}(MoO_4)_5$ single crystals were obtained and their crystal structures were determined [1–9].

The purpose of this work is to study the possibility of forming triple molybdates $Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3$ and $AgA_3Ga(MoO_4)_5$ (A = Mn, Co, Zn, Ni) and investigate crystal structure and electrophysical properties of the obtained compounds.

Experimental

The initial materials were simple molybdates of silver, manganese, cobalt, zinc, nickel, MoO_3 and Ga_2O_3 (reagent grade).

Ag_2MoO_4 and molybdates of divalent metals were obtained by the step annealing of stoichiometric mixtures of $AgNO_3$ (analytical grade), MnO, $Co(NO_3)_2{\cdot}6H_2O$, ZnO, MoO_3 (all chemically pure), NiO (reagent grade) at 350–450 °C (Ag_2MoO_4), 400–750 °C ($MnMoO_4$), 300–700 °C ($CoMoO_4$), 500–700 °C ($ZnMoO_4$), 450–750 °C ($NiMoO_4$) in the air with intermittent grindings every 15 hours for better sample homogenization. Power X-ray diffraction (PXRD) patterns of the prepared compounds do not contain reflections of starting or impurity phases. PXRD and thermal characteristics of all prepared compounds agree well with corresponding data reported in [10–15].

Sample compositions $Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3$ ($0 \le x \le 0.7$, $\Delta x = 0.1$) and $AgA_3Ga(MoO_4)_5$ were prepared by the annealing of appropriate stoichiometric mixtures of Ag_2MoO_4, $AMoO_4$, MoO_3 and Ga_2O_3. The initial mixtures were annealed starting at 300 °C followed by raising the temperature by 20–50 °C (in some cases, 5–10 °C) with intermittent grindings every 20–30 hours for sample homogenization. The calcination time at each temperature was 30–70 h. The phase composition of the obtained products was controlled by the PXRD analysis before each increasing of the annealing temperature.

PXRD patterns were collected at room temperature on a Bruker D8 ADVANCE diffractometer using Cu Kα radiation in the 2θ range from 5° to 100° with a step of 0.02076°. Possible impurity phases were checked by comparing their PXRD patterns with those in the Powder Diffraction File. The crystal structure refinement was carried out with the GSAS [16] program suite using PXRD data. Lattice parameters and individual scale factors were established, and five common peak-shape parameters of the pseudo-Voigt function (No. 2), one asymmetry parameter and one parameter for the zero-point correction were used to describe the powder patterns. The background level was described by a combination of 15-order Chebyshev polynomials. Isotropic displacement parameters (Uiso) were refined, and grouped by chemical similarity by used constrains.

Thermoanalytic studies were carried out on a STA 449 F1 Jupiter NETZSCH thermoanalyser (Pt crucible, heating rate of 10 °C/min in Ar stream).

Ceramic disks for dielectric investigations were prepared by the calcination of pressed powder at 600 °C for 2 h. The disks were of 9–10 mm in diameter and

1–2 mm thick, the electrodes were deposited by painting the disk bases with colloid platinum followed by subsequent one hour annealing at about 580 °C. The direct current (DC) electric conductivity was measured with a V7–38 microammeter. To study the ion transfer, electrical conductivity was measured on an alternating current (AC) by the two-contact method in the frequency range 1 Hz–1 MHz in the temperature range 25–560 °C at the rate of 4 °C/min at both heating and cooling using a Novocontrol Beta-N impedance analyzer. The activation energy of electrical conductivity was calculated from the slope of the straight lines corresponding to the Arrhenius dependence in $\lg(\sigma T) - (10^3/T)$ coordinates.

Results and discussion

PXRD characteristics

The presence of NASICON-like phases in the Ag_2MoO_4–$AMoO_4$–$Ga_2(MoO_4)_3$ systems was determined according to PXRD analysis of samples $Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3$ ($0 \le x \le 0.7$, $\Delta x = 0.1$) which were annealed in the temperature range from 300 °C to melting point. The final annealed temperature was 550–700 °C and depended on both the composition of the reaction mixtures and the nature of the divalent metal. It was established that, despite the close values of the Al^{3+} (0.53) and Ga^{3+} (0.62 Å [17]) radii, gallium containing triple molybdates with NASICON-like structure, apparently, do not exist. All our attempts to obtain rhombohedral phases $Ag_{1-x}A_{1-x}Ga_{1+x}(MoO_4)_3$ by solid state synthesis did not lead to a positive result, probably this is due to the low reactivity of gallium in the molybdate systems. Thus, the simple gallium molybdate $Ga_2(MoO_4)_3$ has not yet been obtained by ceramic technology, and only recently it was synthesized by the sol-gel method [18]. Besides, silver-gallium double molybdate is not synthesized either by ceramic technology or by co-precipitation. In [19] this compound was obtained by the calcining of mixtures of $AgNO_3$, Ga_2O_3, MoO_3 (in ratio 2:1:4) at 350–400 °C for 8–10 h, followed by cooling, homogenization, and the repeated 12–20 hours annealing at 500–550 °C, but the PXRD data of the product are not given by the authors. It should be noted that in none of the later publications (including those of the same authors) additional information about this compound was found.

At the same time, in the Ag_2MoO_4–$AMoO_4$–$Ga_2(MoO_4)_3$ systems triple molybdates of composition $AgA_3Ga(MoO_4)_5$ were found. These compounds were synthesized by the solid-state reactions at 550–600 °C (A = Mn), 540–550 °C (A = Zn), 500–530 °C (A = Co) for 80–100 h. However, nickel-containing compound was not obtained in the single-phase state, even after sintering at temperatures as high as 600–650 °C for 250–300 hours. This may be due to the smallest radius of Ni^{2+} cation (0.69 Å for CN = 6 [17]) in the studied series of simple molybdates of divalent metals.

The triple molybdates $AgA_3Ga(MoO_4)_5$ (A = Zn, Mn, Co) were found to melt incongruently at temperatures of 644, 727, and 739 °C, respectively.

The powder XRD patterns of as-prepared single-phase compounds $AgA_3Ga(MoO_4)_5$ are similar and show that these oxides are isostructural to triclinic $NaMg_3In(MoO_4)_5$ (sp. gr. $P\bar{1}$, Z = 2) [20]. The diffractograms of the $AgA_3Ga(MoO_4)_5$ (A = Mn, Co, Zn) were indexed with taking into account our data obtained earlier in the course of single-crystal structure de-

termination of $AgMg_3R(MoO_4)_5$, R = Fe, Cr [7]. The result of indexing the PXRD patterns for $AgA_3Ga(MoO_4)_5$ (A = Mn, Co, Zn) are given in Table 1. Unit-cell parameters are listed in Table 2.

Crystal structure of $AgZn_3Ga(MoO_4)_5$

The crystal structure of $AgZn_3Ga(MoO_4)_5$ was refined according to the Rietveld method [21], starting with the atomic coordinates of $AgMg_3Fe(MoO_4)_5$ structure [7]. Crystal data, data collection and structure refinement details are summarized in Table 3. Experimental, theoretical, and difference PXRD patterns for the $AgZn_3Ga(MoO_4)_5$ are shown in Figure 1. The fractional

Table 1

The calculated and observed values of PXRD data for $AgA_3Ga(MoO_4)_5$ (A = Mn, Zn, Co)

h	k	l	$AgMn_3Ga(MoO_4)_5$			$AgZn_3Ga(MoO_4)_5$			$AgCo_3Ga(MoO_4)_5$		
			I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°	I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°	I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°
0	0	2	3	9.861	9.850	2	9.981	9.991	2	10.006	10.019
0	1	0	1	12.782	12.767	1	12.954	12.945	1L	12.956	12.943
1	0	0	9	12.903	12.894	9	13.058	13.064	9	13.112	13.108
0	1	1							1L	13.769	13.750
1	0	1	1L	13.654	13.637	1	13.778	13.808	1L	13.853	13.849
0	–1	1				1L	14.021	13.998	1L	14.005	14.017
–1	0	1	1L	13.974	13.977	2	14.170	14.175	1	14.231	14.226
0	0	3	1L	14.805	14.798	1	15.010	15.011	1L	15.061	15.052
1	0	2	1	15.924	15.959	1L	16.154	16.157	1	16.177	16.200
0	–1	2	1L	16.388	16.393	1L	16.577	16.576	1	16.625	16.619
–1	0	2	1L	16.529	16.538	1L	16.799	16.783	1L	16.819	16.844
1	1	1				1L	17.079	17.075			
–1	–1	1				1L	17.541	17.562	1L	17.596	17.610
1	1	2	1L	18.728	18.728						
1	0	3	1L	19.304	19.310						
–1	–1	2	2	19.638	19.630	3	19.826	19.822	3	19.892	19.891
0	0	4	1	19.780	19.774				1L	20.127	20.115
–1	1	0			19.792	1L	20.115	20.122			20.154
–1	0	3	1L	20.025	20.033	1L	20.340	20.336			
–1	1	1	1L	20.406	20.425	1L	20.774	20.790	1L	20.819	20.817
1	1	3	3	21.572	21.577	4	21.846	21.856	5	21.861	21.864
1	–1	2	6	22.117	22.117	10	22.419	22.427	10	22.483	22.482
–1	–1	3				1	22.959	22.996	1L	23.048	23.085
1	0	4	3	23.267	23.270	3	23.569	23.573	3	23.646	23.631
0	1	4			23.265	2	23.662	23.668	1	23.695	23.675
0	–1	4	1	23.959	23.944	10	24.193	24.222	3	24.313	24.306
–1	0	4	1	24.086	24.078	2	24.441	24.445	1	24.511	24.529
0	0	5	100	24.793	24.787	100	25.145	25.148	86	25.221	25.218
–1	1	3	6	24.869	24.848	16	25.307	25.312	16	25.344	25.346

h	k	l	$AgMn_3Ga(MoO_4)_5$			$AgZn_3Ga(MoO_4)_5$			$AgCo_3Ga(MoO_4)_5$		
			I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°	I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°	I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°
1	1	4	3	25.122	25.119	5	25.459	25.465	6	25.480	25.478
0	2	0	3	25.701	25.697	2	26.072	26.058	2	26.055	26.054
2	0	0	73	25.959	29.954	83	26.307	26.302	100	26.396	26.392
0	2	1	23	26.036	26.025	38	26.417	26.422			26.403
2	0	1	10	26.255	26.250	20	26.596	26.590	18	26.679	26.676
0	−2	1	6	26.337	26.333	22	26.664	26.674	7	26.697	26.690
−1	−1	4	4	26.483	26.488	7	26.780	26.782	7	26.888	26.890
1	2	0	8	26.613	26.601	3	26.883	26.881			26.892
−2	0	1			26.614	7	26.984	26.984	7	27.079	27.081
1	2	1	11	26.835	26.829	25	27.132	27.137	18	27.133	27.131
2	1	1	2	27.007	27.001	5	27.283	27.278	3	27.350	27.345
−1	−2	1	11	27.307	27.306	26	27.575	27.575	19	27.613	27.609
0	2	2			27.285	4	27.712	27.731	3	27.705	27.703
−2	−1	1	3	27.507	27.503	4	27.790	27.784	3	27.880	27.879
0	1	5	6	27.622	27.611	10	28.081	28.084	8	28.109	28.105
0	−2	2	3	27.874	27.873	6	28.208	28.210	5	28.255	28.250
1	2	2	2	27.961	27.970	4	28.320	28.322	4	28.308	28.304
1	−1	4	2	28.066	28.064	6	28.423	28.425	5	28.512	28.510
2	1	2	2	28.114	28.121			28.423	3	28.454	28.481
−2	0	2	2	28.164	28.167	1	28.567	28.573	2	28.672	28.678
0	−1	5	6	28.342	28.336	16	28.678	28.676	13	28.782	28.778
−1	0	5				1	28.893	28.900	1	29.000	28.997
−1	−2	2	1	28.877	28.882	2	29.163	29.159	1	29.223	29.217
−2	−1	2	4	29.081	29.082	10	29.391	29.390	9	29.499	29.501
0	2	3	3	29.376	29.367	4	29.859	29.869	3	29.837	29.839
2	0	3	1L	29.525	29.516	2	29.898	29.888	1	29.985	29.973
0	0	6	1	29.860	29.850	1	30.300	30.287	1	30.383	30.372
1	2	3	1L	29.929	29.927	1	30.365	30.334	1	30.324	30.310
2	1	3	4	30.055	30.056	9	30.397	30.397	9	30.453	30.450
0	−2	3	1L	30.175	30.189	1	30.527	30.539	1	30.590	30.603
−2	0	3	1L	30.513	30.488	1	30.983	30.940	1L	31.055	31.055
−1	−1	5	1L	30.622	30.621			30.981	1	31.088	31.106
−1	2	0	1	30.953	30.949	2	31.460	31.462	1	31.483	31.484
−1	−2	3	2	31.213	31.207	4	31.501	31.509	4	31.594	31.592
−2	1	0				1	31.618	31.616	1L	31.691	31.698
−2	−1	3				2	31.748	31.755	18	31.865	31.883
−1	2	1	8	31.303	31.304	22	31.849	31.854			31.865

Continuation of table 1

h	k	l	$AgMn_3Ga(MoO_4)_5$			$AgZn_3Ga(MoO_4)_5$			$AgCo_3Ga(MoO_4)_5$		
			I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°	I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°	I/I_0	$2\theta_{obs.}$,°	$2\theta_{cal.}$,°
1	–2	1	2	31.408	31.410	2	31.912	31.899	3	31.945	31.935
2	–1	1	1	31.440	31.428			31.914	1	31.996	31.999
1	–1	5	1	31.853	31.857	3	32.264	32.264	2	32.362	32.364
–1	1	5	1L	31.974	31.980				1	32.590	32.619
0	2	4	2	32.137	32.125	9	32.653	32.689	2	32.654	32.663
2	0	4	4	32.239	32.238			32.647	6	32.741	32.736
2	–1	2	1	32.512	32.535	11	33.027	33.015	1	33.127	33.106
1	2	4	3	32.569	32.567			33.038	7	33.020	33.014
1	–2	2	3	32.655	32.656	5	33.131	33.133	4	33.188	33.186
0	–1	6				2	33.363	33.368			
0	–2	4	7	33.135	33.134	16	33.511	33.513	11	33.603	33.601
2	2	0	1	33.214	33.200			33.510	1	33.551	33.568
2	2	1	2	33.311	33.313	6	33.634	33.641	5	33.683	33.681
–2	0	4	1	33.426	33.434	4	33.935	33.941	1	34.059	34.066
1	1	6	1L	33.460	33.454			33.948			
–2	–2	1	3	33.847	33.852	11	34.158	34.160	8	34.239	34.239

Cu *K*α1 radiation (l = 1.54056 Å)

Table 2

Unit-cell parameters for $AgA_3Ga(MoO_4)_5$ (A = Mn, Zn, Co)

A	*a*, Å	*b*, Å	*c*, Å	α°	β°	γ°	*V*, Å^3
Mn	6.9844 (3)	7.0519 (4)	17.9700 (8)	87.796 (4)	87.529 (5)	79.386 (4)	868.71
Zn	6.9037 (3)	6.9639 (4)	17.7147 (8)	88.107 (4)	87.440 (4)	78.982 (4)	834.87
Co	6.8810 (4)	6.9657 (4)	17.669 (1)	87.895 (5)	87.344 (5)	78.976 (5)	830.04

atomic coordinates, isotropic atomic displacement parameters, cation occupancies and main selected interatomic distances are presented in Tables 4 and 5. The populations of four independent positions M = (Zn, Ga) and three incompletely occupied Ag sites were refined with keeping the electrical neutrality of the chemical formula. The final compositions of the crystals are close to stoichiometric $AgZn_3Ga(MoO_4)_5$ with a negligible silver deficiency.

In the structure $AgZn_3Ga(MoO_4)_5$ all atoms are located in general positions. Coordination polyhedra of Mo atoms are tetrahedra with Mo–O distances of 1.714–1.824 Å, which are similar to the values found in other molybdates containing a tetrahedral anion. Cations Zn^{2+} and Ga^{3+} are statistically distributed on octahedral positions $M1$–$M4$ with the (Zn, Ga)–O bond lengths of 1.940–2.129 Å. Both Ag1 and Ag3 cations are coordinated by four O atoms (Ag1–O 2.358 Å, Ag3–O 2.415 Å), while Ag2 cation has CN = 5 (Ag2–O 2.495 Å). The structure of $AgZn_3Ga(MoO_4)_5$ consists of MoO_4 tetrahedra, couples of edge-shared $M(1)O_6$ octahedra, and trimers of edge-shared $M(2)O_6$, $M(3)O_6$ and

Table 3

Crystal data and structure refinement for $AgZn_3Ga(MoO_4)_5$

Structural formula	$AgZn_3Ga(MoO_4)_5$
Formula weight, M_r (g mol^{-1})	1172.58
Temperature (K)	298(2)
Crystal system, space group (#)	Triclinic, $P\bar{1}$ (2)
Unit-cell parameters:	
a (Å)	6.9035 (5)
b (Å)	6.9643 (5)
c (Å)	17.7160 (14)
α (°)	88.1039 (11)
β (°)	87.4338 (12)
γ (°)	78.9880 (9)
Unit-cell volume, V (Å^3)	835.0 (2)
Formula unit, Z	2
Calculated density, ρ_{cal} (g cm^{-3})	4.66
Refinement R factors and goodness of fit:	
wR_p	0.0511
R_p	0.0382
R_{exp}	0.0152
$R(F^2)$	0.05815
χ^2	3.40

Table 4

Structural parameters for $AgZn_3Ga(MoO_4)_5$

Atom	**Occupancy**	***x***	***y***	***z***	***Uiso***
Mo1	1	0.2722(8)	0.3095(8)	0.5282(3)	0.030(2)
Mo2	1	0.2129(8)	0.8293(9)	0.2856(3)	0.028(2)
Mo3	1	0.6843(8)	0.2187(8)	0.3109(3)	0.023(2)
Mo4	1	0.2811(9)	0.0522(9)	0.9044(3)	0.029(2)
Mo5	1	0.2520(8)	0.5491(8)	0.0863(3)	0.021(2)
*M*1	0.788(1)Zn+0.212(1)Ga	0.1834(12)	0.8241(11)	0.4938(5)	0.0126(3)
*M*2	0.901(1)Zn+0.099(1)Ga	0.1704(14)	0.0855(16)	0.1145(5)	0.045(4)
*M*3	0.798(1)Zn+0.202(1)Ga	0.7829(12)	0.4310(13)	0.1239(4)	0.014(3)
*M*4	0.505(1)Zn+0.495(1)Ga	0.2546(12)	0.3014(13)	0.7370(4)	0.023(3)
Ag1	0.323(3)Ag	0.149(3)	0.339(3)	0.2857(12)	0.062(5)
Ag2	0.328(3)Ag	0.122(4)	0.308(4)	0.3155(13)	0.062(5)
Ag3	0.342(3)Ag	0.097(3)	0.370(3)	0.3445(11)	0.062(5)
O1	1	0.511(5)	0.194(5)	0.5163(18)	0.015(1)
O2	1	0.289(4)	0.366(4)	0.6238(17)	0.015(1)
O3	1	0.171(4)	0.545(5)	0.4601(18)	0.015(1)
O4	1	0.130(5)	0.126(5)	0.4978(18)	0.015(1)

Continuation of table 4

Atom	Occupancy	*x*	*y*	*z*	*Uiso*
O5	1	0.189(4)	0.872(4)	0.3866(18)	0.015(1)
O6	1	0.477(5)	0.719(4)	0.2580(17)	0.015(1)
O7	1	0.140(5)	0.053(5)	0.2220(19)	0.015(1)
O8	1	0.098(5)	0.641(5)	0.2687(18)	0.015(1)
O9	1	0.419(5)	0.280(4)	0.3590(17)	0.015(1)
O10	1	0.804(5)	0.191(4)	0.3830(18)	0.015(1)
O11	1	0.681(5)	0.995(5)	0.2696(17)	0.015(1)
O12	1	0.774(4)	0.370(5)	0.237(2)	0.015(1)
O13	1	0.198(4)	0.121(4)	0.997(2)	0.015(1)
O14	1	0.468(5)	0.040(4)	0.0841(15)	0.015(1)
O15	1	0.831(5)	0.202(5)	0.1174(16)	0.015(1)
O16	1	0.238(4)	0.305(5)	0.8544(17)	0.015(1)
O17	1	0.249(4)	0.546(4)	0.987(2)	0.015(1)
O18	1	0.485(5)	0.488(5)	0.1153(17)	0.015(1)
O19	1	0.171(4)	0.778(5)	0.1292(18)	0.015(1)
O20	1	0.097(4)	0.410(5)	0.1173(18)	0.015(1)

$M(4)O_6$ octahedra, which are linked by the common vertices to form a 3D framework (Fig. 2). In the large framework cavities, the silver cations are disordered on three close positions with the distances Ag–Ag 0.595(4) Å and 1.101(2) Å.

Such a disordering is also typical of other compounds of this isostructural series [7, 9], suggesting a possible mobility of the Ag^+ cations in the compounds. This is favored not only by defects in Ag positions along with their irregular coordina-

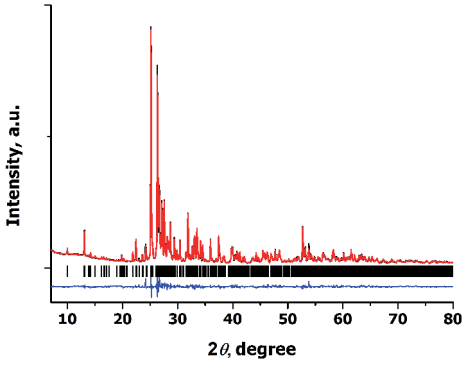

Fig. 1. Observed (black line) and calculated (red line) XRD patterns of $AgZn_3Ga(MoO_4)_5$. Vertical bars indicate the positions of the Bragg peaks. The lower trace depicts the difference between the experimental and calculated intensity values

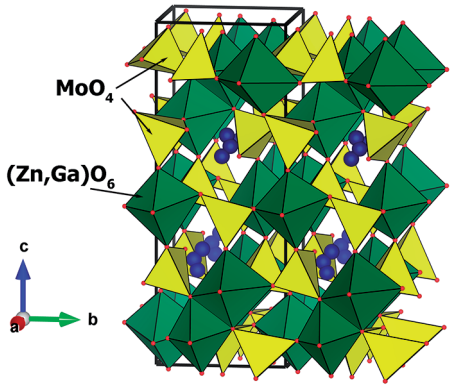

Fig. 2. Projection views of the structure of $AgZn_3Ga(MoO_4)_5$ along the *a* axis. The blue spheres and small red spheres indicate Ag and oxygen atoms, respectively

Table 5

Selected interatomic distances(Å) in $AgZn_3Ga(MoO_4)_5$

Mo1-tetrahedron		**Mo2-tetrahedron**	
Mo1–O1	1.696(3)	Mo2–O5	1.819(3)
–O2	1.764(3)	–O6	1.889(3)
–O3	1.726(3)	–O7	1.891(3)
–O4	1.858(3)	–O8	1.698(3)
<Mo1–O>	1.761	<Mo2–O>	1.824
Mo^3-tetrahedron		**Mo4-tetrahedron**	
Mo3–O9	1.961(3)	Mo4–O13	1.749(3)
–O10	1.739(3)	–O14	1.726(2)
–O11	1.747(4)	–O15	1.922(3)
–O12	1.812(3)	–O16	1.760(3)
<Mo3–O>	1.815	<Mo4–O>	1.789
Mo5-tetrahedron		***M*1-octahedron**	
Mo5–O17	1.758(4)	*M*1–O1	2.092(3)
–O18	1.683(3)	–O3	2.068(3)
–O19	1.773(3)	–O10	2.186(3)
–O20	1.640(3)	–O4	2.070(2)
<Mo5–O>	1.714	–O5	1.918(3)
		–O4	2.124(3)
		<*M*1–O>	2.076
***M*2-octahedron**		***M*3-octahedron**	
*M*2–O7	1.918(3)	*M*3–O18	2.030(3)
–O13	2.096(3)	–O17	1.99(4)
–O19	2.144(3)	–O15	1.572(3)
–O20	2.224(3)	–O16	1.869(3)
–O14	2.066(3)	–O12	2.038(3)
–O15	2.325(3)	–O20	2.143(3)
<*M*2–O>	2.129	<*M*3–O>	1.940
***M*4-octahedron**		**Ag1-polyhedron**	
*M*4–O8	2.398(4)	Ag1–O9	2.29(4)
–O11	2.033(4)	–O8	2.080(3)
–O2	2.053(3)	–O7	2.33(4)
–O6	1.837(3)	–O12	2.73(4)
–O16	2.079(3)	<Ag1–O>	2.358
–O12	2.320(3)		
<*M*4–O>	2.120		
Ag2-polyhedron		**Ag3-polyhedron**	
Ag2–O9	2.19(4)	Ag3–O9	2.22(4)
–O10	2.70(4)	–O8	2.28(4)
–O8	2.41(4)	–O10	2.62(4)
–O7	2.45(4)	–O3	2.540(3)
–O12	2.725(3)	<Ag3–O>	2.415
<Ag2–O>	2.495		
Ag1–Ag2	0.595(4)		
Ag1–Ag3	1.101(2)		

tion, but also a rather flexible polyhedral framework of the $NaMg_3In(MoO_4)_5$ structure type, which involves interconnected cavities.

Electrophysical properties

As was noted in the previous section, the structural features of the obtained molybdates allow us to expect these compounds to have the increased ionic conductivity. This was already confirmed by us in the case of $AgMg_3Al(MoO_4)_5$ ($\sigma = 2.5 \times 10^{-2}$ S/cm) and $AgMn_3Al(MoO_4)_5$ ($\sigma = 7.1 \times 10^{-3}$ S/cm) at 500°C [7]. In this work as an example, the results of studying electrophysical properties for $AgMn_3Ga(MoO_4)_5$ are presented.

It was found that the DC conductivity of ceramic sample $AgMn_3Ga(MoO_4)_5$, measured with the V7–38 device, is negligible as compared to the ac conductivity (Fig. 3) in temperature region of 100–560°C. As the platinum electrodes are blocking in the DC conductivity measurement mode, the DC conductivity of $AgMn_3Ga(MoO_4)_5$ corresponds to the electronic one. Therefore, it can be concluded that the AC conductivity is almost equal to the ionic one.

It is seen that near room temperature the conductivity is as small as 10^{-7} S/cm

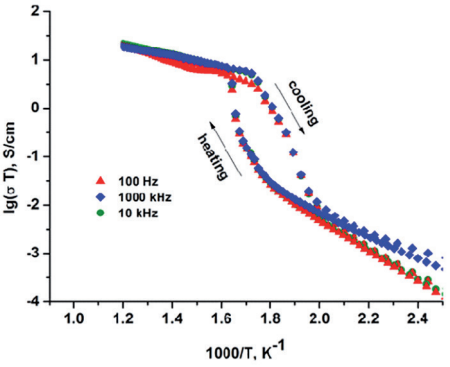

Fig. 3. Temperature dependences of the ionic conductivity on heating and cooling for $AgMn_3Ga(MoO_4)_5$

but quickly rises with temperature to values of about 10^{-2} S/cm. It is noteworthy that the conductivity in $AgMn_3Ga(MoO_4)_5$ increases with temperature in non-monotonic way showing distinct breaks on $\lg\sigma = f(1/T)$ curves at 310 °C. Above these temperature the $\lg\sigma = f(1/T)$ dependences are almost linear with the small activation energy value $E_a = 0.26$ eV. Above 310°C, the ionic conductivity of $AgMn_3Ga(MoO_4)_5$ increases up to $2.03 \cdot 10^{-2}$ S/cm at 500°C, which is close to the corresponding characteristics of the known ionic conductors.

Conclusions

The possibility of the formation of silver-containing gallium triple molybdates with Mn, Co, Zn, Ni, analogous to the phases $Ag_{1-x}A_{1-x}R_{1+x}(MoO_4)_3$ and $AgA_3R(MoO_4)_5$ obtained by us in the Ag_2MoO_4–$AMoO_4$–$R_2(MoO_4)_3$ (A = Mg, Co; R = Al; A = Mg, R = In) systems, was studied. It was shown that in the Ag_2MoO_4–$AMoO_4$–$Ga_2(MoO_4)_3$ (A = Mn, Co, Zn, Ni) systems the NASICON-like phases of the composition $Ag_{1-x}A_{1-x}R_{1+x}(MoO_4)_3$ are not formed. The triple molybdates of the composition $AgA_3Ga(MoO_4)_5$ (A = Mn, Co, Zn) were synthesized and characterized. $AgNi_3Ga(MoO_4)_5$ was not obtained in the single-phase state. It was established that the obtained compounds incongruently melt and belong to the structural type of triclinic $NaMg_3In(MoO_4)_5$ (sp. gr. $P\bar{1}$, Z = 2). The structure of the obtained compounds was refined by the Rietveld method using the powder diffraction data for $AgZn_3Ga(MoO_4)_5$. The structural features of the obtained molybdates allow us to expect these compounds to have the increased ionic conductivity. This was

confirmed by studying electrophysical properties of $AgMn_3Ga(MoO_4)_5$. It was shown that the high-temperature electrical conductivity of this compound reaches 10^{-2} S/cm at E_a = 0.26 eV, which is close to the corresponding characteristics of the known ionic conductors.

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